6. THERMODYNAMICS

STUDY NOTES

[1SAQ]

THERMODYNAMICS means **FLOW of HEAT**

Thermodynamics deals with the 'Heat Energy changes' in Chemical processes.

HEAT(q)

Heat is a form of energy. It flows between system and surroundings due to difference in temperatures.
Ex: Heat flows from Sun to Earth, Food is converted into Heat and is used to do work.

I) TYPES OF THERMODYNAMIC SYSTEMS

1) Open system

It is the system which can 'exchange both heat energy and matter' with its surroundings.
It allows inputs into it. **Ex:** A Hot cup of Tea in a saucer, Human Body.

2) Closed system

It is the system which can 'exchange only heat energy but not matter' with its surroundings.
It doesn't allow any inputs into it. **Ex:** Chilled sealed Pepsi bottle.

3) Isolated system

It is the system which 'can't exchange either heat energy or matter ' with its surroundings.
Ex: Hot Coffee in a thermos flask.

II) TYPES OF THERMODYNAMIC PROCESSES

1) Isothermal process

It is a Thermodynamic process in which temperature remains constant.
This occurs when the system is in contact with the surroundings.
Ex: Our body temperature is kept isothermally at 98.6ºC. Latent heat of melting of ice at 0ºC.

2) Adiabatic process

It is a Thermodynamic process in which heat (q=0) is neither gained nor lost between the system and surroundings.
In Adiabatic process entire internal energy(ΔU) is utilized to do work(w) ($\because$ q=0)
Ex: Fast and Quick processes involved in Nozzles, Compressors, Turbines.

3) Spontaneous process

Spontaneous processes (i) occur naturally (ii) are not driven by external agents.
(iii) follow only one direction. (iv) are exothermic and loose energy
(v) enhance entropy and have negative 'Gibbs free energy'.
Ex: Flow of heat from Sun to Earth, Flow of rivers from Mountains to Sea, Combustion, Melting of Ice at room temperature and atm pressure.

4) Non-Spontaneous process:

Non-spontaneous processes are driven by external agents.
Ex: Water will not freeze into Ice spontaneously at room temperature and atm pressure.

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Chemistry THERMODYNAMICS Vs **Physics THERMODYNAMICS**

1) In Chemistry, work done on the system is positive; in Physics, work done by the system is positive.
2) In Chemistry we have Chemical Equations, Entropy, Gibbs energy; in Physics Heat engine.
3) First law of Thermodynamics in Chemistry, $\Delta U = q + w$; in Physics we write, $q = \Delta U + w$
Both statements convey the same meaning but with few changes in notations and signs.

III) TYPES OF THERMODYNAMIC REACTIONS

1) Exothermic reactions

These are reactions(chemical) which release Heat(light, sound) into surroundings.

Ex: Cavemen made fire by striking rocks, Explosion of bomb,
Nuclear fusion reactions of H into Helium in Sun, formation of chemical bonds in compounds.....

In exothermic reactions H_P is less than H_R. So, ΔH is negative.

Ex: $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -393.5$ KJ

2) Endothermic reactions

These are reactions (chemical) which absorb Heat energy .

Ex: Photosynthesis in plants, melting of ice cubes, evaporation of water,
breaking of chemical bonds, cooling our body from fans & ACs

In endothermic reactions, H_P is greater than H_R. So, ΔH is positive.

IV) PROPERTIES OF SYSTEMS

1) Extensive properties

These are the properties which depend on the total amount of the material present in the system.
These are mass dependent properties.

Ex: Weight,Volume, Internal energy, Heat

2) Intensive properties

These are mass independent properties.

Ex: Pressure, Temperature, Specific heat, Density, Refractive index, Viscosity, Surface tension.

3) Specific heat (s)

It is the amount of Heat required to raise the temperature of '1 gram of substance' through 1ºC

4) Heat capacity (C)

It is the amount of heat required to raise the temperature of 'entire substance' through 1ºC.

5) Heat capacity at constant volume (C_v)

C_v is the change in Heat capacity (internal energy) of the gas at constant volume.

6) Heat capacity at constant pressure (C_p)

C_p is the change in Heat capacity (internal energy) of the gas at constant pressure.

Relation between C_p and C_v i) $C_p - C_v = R$ ii) $C_p/C_v = \gamma$

7) Hess's law

The 'total heat change in a reaction' is the same whether
the chemical reaction takes place in one single step or in several steps.

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A Wonderful Kitchen Q to differentiate Heat Vs Specific heat Vs Heat Capacity

Question: మీ Kitchen లో నాలుగు రకాల Cooking Vessels, రెండు Sizes లో ఉన్నాయనుకోండి! అవి
a) 1 Kg Clay vessel **b)** 1 Kg Copper vessel **c)** 1 Kg Steel vessel **d)** 2 Kg Steel vessel
ఒక్కోదానిలో ఒక **Half kg Rice** ను ఒకేసారి **Cook** చేస్తే ఏ **Vessel** లో వంట **Fast** గా అవుతుంది?
[Given data: Specific Heats: For Clay 878J/kg; Copper 385J/kg ; Steel 420J/kg]

Answer: All the 4 Vessels require **Heat** to cook.

Among the given, **Specific** గా చూస్తే **Specific Heat** of Copper is low. కాబట్టి Copper vessel requires less heat to raise its temperature to 1ºC when compared to others. ఇంకా అన్నింటికంటే పెద్దదైన 2kg Steel vessel నకు **Heat capacity** ఎక్కువ. అది వేడెక్కడానికే ఎక్కువ సమయం కావాలి.

So, **1 kg Copper Vessel** b takes **lesser time** to cook.

RIDDLE QUESTION TO U:

Which Vessel takes much longer time to cook? Is it a (or) c (or) d ?

FOUR STATE VARIABLES OF GASEOUS SYSTEM

The four state variables (functions) that determine the state of gaseous system are Pressure(P), Temperature (T), Volume (V), Amount of substance (n).
Their values depend only on the initial and final states of the system, but not on the path of the reaction.

FOUR STATE VARIABLES OF THERMODYNAMIC SYSTEM:

Internal energy (U), Enthalpy(H), Entropy(S), Gibbs energy (G).

1) Internal energy change (ΔU)

It is the energy stored in the form chemical, electrical, mechanical or any other form in a system, at constant temperature and volume.

2) Enthalpy change (ΔH)

It is the amount of heat exchanged by a system with its surroundings at constant pressure & temperature
(i) Enthalpy change measured at constant pressure is given by $q_p = \Delta H$.
(ii) Enthalpy change measured at constant volume is given by $q_v = \Delta U$.

3) Entropy (S) [Units: J/K]

Entropy is a measure of disorder or randomness of molecules of the substance.
Entropy is a thermodynamic property. Entropy is an extensive property.
Order of Entropy: $S_{vapour} > S_{liquid} > S_{solid}$
For a spontaneous change $\Delta S > 0$.

4) Gibbs energy(G)

Gibbs energy relates entropy and enthalpy change.
It is the amount of the energy available from a system which can be put to useful work at constant temperature and pressure. $G = H - TS \Rightarrow \mathbf{\Delta G = \Delta H - T\Delta S}$.
For a spontaneous change $\Delta G < 0$.(negative)
For a non-spontaneous change $\Delta G > 0$. (positive)
For equilibrium reactions $\Delta G = 0$.

LAWS OF THERMODYNAMICS

First law of thermodynamics (Law of conservation of energy):
"The energy in a process is neither created nor destroyed" but it may be transferred from one form into the other. **Mathematical form:** $\Delta U = q + w$.

Statements of II law of thermodynamics:
Heat can not flow from a colder body to a hotter body on its own.

Third law of thermodynamics
"The entropy of a pure and perfectly crystalline substance approaches zero, when the temperature approaches absolute zero."

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Thermodynamics లో ముగ్గురు మిత్రులు: q (Heat), ΔU(Energy change), w (work)
First Law of Thermodynamics: q= ΔU + w
Total Input energy = Total output (Thus energy is conserved)
1000 calories energy ఉన్న Food(q-Carbohydrates) ను input గా తీసుకొని తిన్నప్పుడు దానిని digest చేసుకోవడానికి 200 units Internal Energy (ΔU) గా ఖర్చు అయితే మిగిలిన 800 units body లోని వివిధ భాగాలకు చేరి ఉత్సాహంగా work(w) చేయడానికి output గా వస్తుంది.
వేడి వేడి భోజనం, వేడి వేడి టీ, కాఫీలను మన Body ఎక్కువగా కోరుకోవడానికి కారణం ఇదే!.
వేడి వేడి Food తినడం వలన Internal Energy కి తక్కువ శక్తి అవసరం అవుతుంది.
కాబట్టి తీసుకున్న Food త్వరగా, తేలికగా digest అవుతుంది.